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# Peroxvite Theory of Superconductivity & Possible Superconductive Organic Formulations

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1988-PREPARED BY SUPERCONDUCTOR  
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'PEROXVITE' is no misspelling of Perovskite type structure assigned to the high  $T_c$  superconductive oxides. The name 'Peroxvite' is coined to try and explain the extension of Heisenberg's uncertainty principle on the certainty that the prediction of the exact location of an electron and its movement in a compound, as well as its "structure", (possibly the location of the nuclei) has a range of uncertainty associated with it. Applying this possible 'Peroxvite' theory, possibilities for designing other higher  $T_c$  inorganic and organic superconductors are shown.

Those who are familiar with organic and polymer conductor synthesis know that most of the dopants used in making the organic compounds get the electrical conductive behavior is by oxidizing them with a suitable oxidants. Majority of the oxidants used to date are group V fluoro compounds ( $AsF_6$ ,  $PF_6$ ,  $TaF_6$ , etc.), oxyhalogens (chlorate, iodate, etc.), as well as iodine and perhenates.<sup>(1)</sup> Some of these exhibit superconductivity near 1 to 5°K. So far, use of oxidants such as peroxides and perthio compositions have not been tried. This article suggests that by trying these peroxide and or perthio compound oxidant doping one can find an organic or polymer superconductor exhibiting high or higher  $T_c$ 's than the  $YBaCuO$  or the  $TlBaCaCuO$  compounds. The reasoning is based on evaluating the present high  $T_c$  compounds with an entirely different structural analysis, which might shock those ingrained with the only one mode of structural analysis... 'perovskite model with  $CuO_2$  layers'.

Most of the studies on high  $T_c$  superconducting oxides, done to date, tend to depict the crystal structure as a distorted 'Perovskite' layered model with a tetragonal to orthorhombic transition. Most of the early works by researchers across the world were done using minuscule particles, closest to single crystals, with the superconducting properties. Only a few single crystal x-ray diffraction studies have been reported so far <sup>(2)</sup>. Most reports indicate an overall unit cell dimension of  $a = b = 3.87 \text{ nm}$  and  $c = 11.715 \text{ nm}$ , or very close to these values, using X-Ray

diffraction, TEM, Electron Spin Resonance, etc.

Assuming this unit cell to contain the superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  molecule, the volume of unit cell comes to  $0.1766 \text{ nm}^3$ : the additive volume of the component elements using their ionic, covalent and atomic radii are  $0.0952$ ,  $0.1144$  and  $0.2857 \text{ nm}^3$  respectively. Thus the percentage packing are  $54.2\%$ , and  $65.2 \%$  based on ionic and covalent volumes of the components respectively. (See Table 1). Most of the published work to date depicts the so called layer structure with holes or defects on a major simplistic and singular assumption that the oxygen species are present only as 'oxide' ions in the matrix; and considerable re-search has been spent in fitting this assumption to experimental measurements. This assumption is the one which is questioned in this article, while presenting plausible alternative reasoning for the superconducting behavior.

Once the basic assumption that the oxygen ion is present as an 'oxide' ion of apparently known 'ionic radius' continues to be used, the extended theories all tend to be one sided. 'Oxide' ion size has to be kept constant in the assumed layered perovskite structure. When this constancy assumption tend to negate other principles of 'electro-neutrality', one or more of the cations get to have an unusually different valency (such as trivalent copper) or the structures get depicted with defects or holes. This unilateral assumption may be in the way of really understanding the fundamental theories of what makes these compounds have higher  $T_c$ 's and how can one design a material having room temperature or still higher temperature superconductivity.

One other method of analyzing the  $\text{YBaCuO}$ ,  $\text{TiCaSrCuO}$ ,  $\text{BiCaSrCuO}$  and the  $\text{BiKBaO}$  systems is presented below, crediting some of the studies that are being done with alternative views.

Let us take a 'radical' or other 'ionic' view, based on stable compounds known from the eighteenth century. In 1799, Humboldt knew about Barium Peroxide. Most of the nineteenth century chemical industries used barium peroxide to generate oxygen and hydrogen peroxide, before liquefaction of air to make oxygen or producing hydrogen peroxide starting with anthraquinone oxidation came to be commercially feasible. Potassium superoxide,  $\text{KO}_2$ , is still used for emergency oxygen generation. In these compounds, oxygen is not present as an 'oxide' ion, with the so called 'divalency' and 0.132-0.140 nm ionic radius.

In peroxides, two oxygen atoms are close together with an inter-oxygen, (O-O), distance of 0.137 nm<sup>(3)</sup> or 0.13 to 0.15 nm<sup>(4)</sup> (compare this dimension with the 0.066 nm atomic radius or 0.072 nm covalent radius of oxygen), and exhibit a divalency together, i.e.  $\text{O}_2^{2-}$ . Two oxygen atoms are close together as two nuts in a single peanut shell, with the outer electron orbit resembling the peanut shell<sup>(4)</sup>. In super oxides, two oxygen atoms have their electronic shell merged closer together than in peroxides, exhibiting a univalence of  $\text{O}_2^-$ , such as in  $\text{KO}_2$ .

The crystal structure of  $\text{BaO}_2$  is a distorted tetragonal type with  $a = b = 0.566$  nm and  $c = 0.672$  nm<sup>(3)</sup>. Its structure is similar to  $\text{BaC}_2$ , barium carbide. Most stable of the peroxides known to date is barium peroxide. Barium oxide picks up oxygen from air at 400°C becoming a peroxide; which melts at 440°C, decomposing only around 800°C and is known to dissolve barium oxide. Other peroxides in the decreasing order of thermal stability include  $\text{Na}_2\text{O}_2$ ,  $\text{SrO}_2$ ,  $\text{CaO}_2$ ,  $\text{MgO}_2$ ,  $\text{Li}_2\text{O}_2$ ,  $\text{R}_2\text{O}_2$  and  $\text{H}_2\text{O}_2$ . Some of the intermediate peroxides are more difficult to form.  $\text{R}_2\text{O}_2$ 's are organic peroxides, where R is an aliphatic or aromatic group.

Not all peroxides are ionic. Rare earth peroxides, such as  $\text{LaO}_2$ ,  $\text{YO}_2$ , etc. are covalent in nature and form less readily. Transition metals hardly ever form true peroxides or superoxides. Most of the apparent trivalent copper compounds never exist without other cations such as K, Ba, Sr or R, all of which are capable of forming peroxides or peroxide hydrates. Thus trivalency of



copper is questionable. Not all peroxo compounds release oxygen or generate hydrogen peroxide in water at the same rate. But all of them are capable of showing oxidation-reduction type reactions, and the interpretation from such aqueous titrations can be misleading in defining a higher unusual valency for one ion or the presence of peroxo or quasi-superoxo compound. The interpretation can only be that there is an oxidation-reduction reaction induced in the complex mixture, which does not follow the conventionally assumed (only in the past 50 years or so) oxide ion behavior.

It is interesting to note that most published X-Ray diffraction studies on YBaCuO systems show only the Y-O, Ba-O, Cu-O distances and not the O-O distance. Similar is the case for the published structural studies in the thallium and bismuth high  $T_c$  compounds. Two of the X-Ray studies <sup>(2,5)</sup>, like most of the studies to date, discuss only the cation-oxygen distance measurements, and conclude some minor distortion in the perovskite structure. The results, of the cation-oxygen distances, although measured with considerable difference in values, eg. 0.176 to 0.245 nm for Cu-O distance, (See Table 2 ) have been averaged to locate the oxygen 'ions' in the unit cell periphery, without questioning that the measurements may be more accurate than interpretation to fit the perovskite structure. One with enough patience and geometric acumen might be able to fit the real measured values, (without simplified averages), to a little more complicated three dimensional structure consisting of some peroxo- or superoxo- groups intermingled with normal divalent oxide ions. Or the structure may have alternating peroxide and oxide layers tied to the different cations. See Figure 1 with discussions shown later in the article.

Such a structure is called 'PEROXVITE' structure by this article, which enables the close proximity of the very large barium atoms - and yttrium atom and somewhat smaller copper atoms or ions of like positive charge to pack in the unit cell with closely bound oxygen atoms or ions sufficiently satisfying the electro-neutrality and still allowing free flow of electrons leading to higher temperature superconductivity.

One might note that the picture could become clearer by depicting the basic nuclei location of each constituent element to fit the measured values to facilitate the electron path. Is Heisenberg's theory good only to predict that only the electrons may be present in a specific orbit with an associated probability? Could it be possible that the nuclei centers may also oscillate in a three-dimensional orbit with certain probability of location associated? Such a certainty of unpredictability should encourage more diversified formulations, similar to the efforts by Bednorz and Mueller recently and other researchers (in the past half a century) who found conductivity in oxides or polymers usually dubbed insulating materials. This presents one more option for theoretical physicists and chemists to ponder about.

Other avenues thus open up in the design of higher  $T_c$  superconductors to pragmatic chemists and engineers, based on this 'PEROXVITE' theory. One such avenue is, fabrication of polyperoxides such as can be done using MEKP (methyl ethyl ketone peroxide) or benzoyl peroxide, common catalysts in plastics formulations. For example, doped or undoped polyperoxides, epoxides, polyperester-polyester or silicones which show structures with high atomic or covalent packing densities might lead to organic superconductors with higher  $T_c$ 's, by using the peroxo or perthio PITSTOPS which are not holes nor defects. Ceramicists specializing in piezo-electrics and semi-conducting oxides have long known the need to control and minimize the oxygen partial pressure in obtaining the desired properties. Catalysis specialists in the field of petroleum refining have long known the oxidation-reduction catalysts and how to formulate them with the help of Mendeleev's periodic table. Bringing some of the understanding that the experts in organic peroxides have to understand the recent high  $T_c$  oxides would further our knowledge. For example, infra-red spectroscopy is commonly used to define the oxygen-oxygen<sup>(4)</sup>, or sulfur-sulfur bond distances by these specialists. Very little work in this line has been pursued in the study of the recent high  $T_c$  oxides.

Basic concepts leading to the 'PEROXVITE' theory by Neelameggham have been published in Let's Levitate <sup>(6,7)</sup>. The work by Sasaki, et al <sup>(8)</sup> presents evidence of copper being present in uni- and di- valent states in YBaCuO, rather than the tri- valency assumed by many. Goodenough <sup>(9)</sup>, mathematically attempted to find the presence of peroxides in YBaCuO using conventional approaches. Wet chemical analyses of YBaCuO compounds have been interpreted in a conflicting manner <sup>(10,11)</sup>.

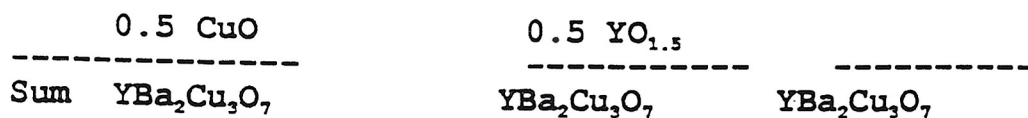
Note that the critical step in making YBaCuO a high  $T_c$  superconductor is oxygen annealing between 450 and 500°C - the temperature at which barium oxide absorbs oxygen to form the peroxide. Note also that all the high  $T_c$  compounds known to date contain Ba, Ca, K or Sr - the peroxide or superoxide formers. Other constituents--- the rare earths can form R.E.O<sub>2</sub> <sup>(12)</sup>, thallium and bismuth can form Tl<sub>2</sub>O<sub>2</sub> or TlO<sub>2</sub> <sup>(13)</sup> or Bi<sub>2</sub>O<sub>4</sub> intermediate covalent peroxides. Pb, Cd, Sb and Sn can form intermediate covalent peroxides and or dioxides and may one day find application in the high  $T_c$  superconductor formulations.

Kao, Johnson Controls Inc., Wisconsin <sup>(14)</sup> was successful in fabricating YBaCuO superconductor using Y<sub>2</sub>O<sub>3</sub>, 4 BaO<sub>2</sub> and 3 Cu<sub>2</sub>O without oxygen annealing. Hepp and Gaier <sup>(15)</sup> showed that with Y<sub>2</sub>O<sub>3</sub>, BaO<sub>2</sub> and CuO starting materials a better homogeneous superconducting compound is formed.

**FIGURE 1.**  
Constituents in Unit Cell Layers of High  $T_c$  YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.

Conventional Perovskite Model with defects???	Kao's Synthesis Peroxvite model 'B'	Peroxvite model 'A'
0.5 CuO	0.5 YO <sub>1.5</sub>	0.5 YO <sub>2</sub>
BaO	0.5 Cu <sub>2</sub> O	CuO
CuO <sub>2</sub>	BaO <sub>2</sub>	BaO <sub>2</sub>
Y	0.5 Cu <sub>2</sub> O	Cu <sub>2</sub> O
CuO <sub>2</sub>	BaO <sub>2</sub>	BaO
BaO	0.5 Cu <sub>2</sub> O	0.5 YO <sub>2</sub>





Looking at 'PEROXVITE A' shown in Figure 1, one can synthesize other alternate substitutions of any of the constituents. For example, the substitutions of CuO with  $\text{TiO}_2$  <sup>(18)</sup>, and with  $\text{ZrO}_2$  <sup>(19)</sup> have been reported without substantially lowering the  $T_c$ ; these substitutions fit model 'A'.

The bond length and structural analyses measurements done to date, on thallium <sup>(20)</sup> and bismuth substitutions for rare earths, do not show the O-O bond length, can also be fitted to the PEROXVITE model shown here, within the unit cell dimensions.

Even the recent work by Cava and Batlogg <sup>(21)</sup>, on the BiKBaO compounds of  $T_c$  near 30°K can be fitted with the 'PEROXVITE' model, without having to undermine the O-O bond lengths. Some of the existing techniques along with the ones presented here, show that the Science of Superconductivity, inspite of the commercial glory attached to it, is still only as good as alchemy of the pre-industrial revolution period and are as tasty as the home-made food by mothers and grandmothers who impart good taste to their concoctions without theorizing.

## SPECULATIONS ON ANALYTICAL STUDIES

The use of computers to reduce the data provided by X-ray instrumentation has made it possible to provide structural information on many substances with much less effort and time than was possible only a few years ago. A return to the days of the mechanical calculator or, shudder, slide rule would certainly cut down on the number of articles discussing the structure of superconducting materials. The hardware-software combinations used for crystallographic research eliminate most of the tedious calculations and even make many decisions about what the data means. The late Robert Heinlein coined the word "TANSTAAFL" to emphasize the idea that "There ain't no such thing as a free lunch". We are all taking advantage of the lunch we get from modern instrumentation but we don't always take the price into consideration. Some people are reporting



findings generated by a computer program that is doing calculations that they have never done by hand. This makes life easier but removes some of the opportunities for the imagination to reach a non routine conclusion. Any computer program reflects to some degree the attitude, methods, and prejudices of the person or persons that wrote it. Data may be disregarded as spurious that has real meaning, a conclusion may be ignored simply because it hasn't been reported before. The significant structural information concerning superconductors may lie outside the procedures used by the software written to classify normal crystalline materials. For example, the term "layered structure" has been used repeatedly to describe superconductors but very little if any work has been done using chromium radiation rather than copper as was the practice for the investigation of layered materials. Could it be because this would require a change in the software? A real breakthrough just might come from an investigator that doesn't have any money for expensive software.

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TABLE 1.

Element	Valence	Ionic Radius nm	Covalent Radius nm	Free Atom Radius nm
Y	+3	0.091	0.162	0.227
Ba	+2	0.135	0.198	0.278
Cu	+2	0.068	0.117	0.157
	+1			
O	-2	0.132	0.073	0.065
Additive Volume, nm <sup>3</sup>		0.095	0.114	0.286
Unit Cell, nm <sup>3</sup>		0.177		
%Packing		54.2	65.2	

TABLE 2.

Interatomic Distances For YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>  
(A) (B)

Ba-O1 (x4)	2.776	(x4)	2.741
-O2 (x2)	2.954	(x2)	2.877
-O3 (x2)	2.951	(x2)	2.949
-O4 (x2)	2.931	(x2)	2.986
-O5 (x2)	2.926	-----	?
mean	2.866		
Y-O4 (x4)	2.404	(x4)	2.387
-O5 (x4)	2.403	(x4)	2.402
mean	2.404		
Cu1-O1 (x2)	1.763	(x2)	1.843
-O2 (x2)	1.933	(x2)	1.942
-O3 (x2)	1.936	(x2)	1.929
mean	1.846		
Cu2-O1 (x1)	2.452	(x1)	2.306
-O4 (x2)	1.945	(x2)	1.958
-O5 (x2)	1.948	-----	?
mean	2.048		

(Other Pertinent Bond Lengths):

Cu-O Bond Lengths 2.66 and 1.97 Å in CuO (C).  
1.85 Å in Cu<sub>2</sub>O (D).

(A). Reference 2. (B). Reference 5.  
(C). Reference 16. (D). Reference 17.